




PCT/US 00 / 27415

100570905 

INVESTOR IN PEOPLE

US00/27415

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

15/4

REC'D 11 DEC 2000

WIPO

PCT

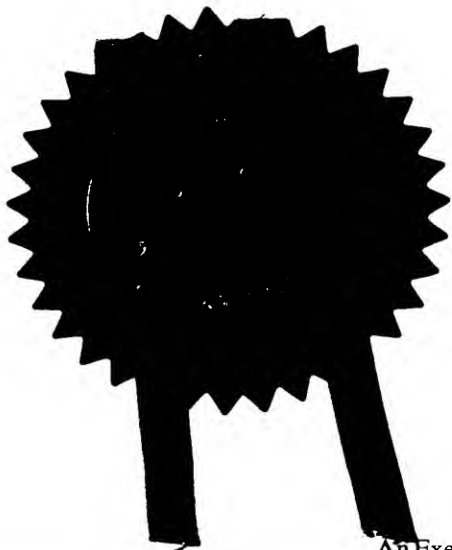
4

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed



Dated

19 OCT 2000

**PRIORITY
DOCUMENT**SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



The
Patent
Office

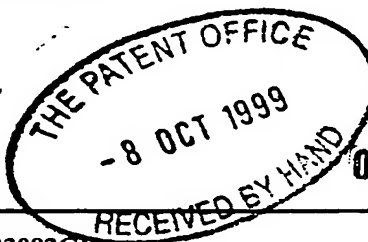
1100759 2482731-1 200012
201/7720 0.00 - 2/1388211

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH



08 OCT 1999

1. Your reference

P023083GB

2. Patent application number

(The Patent Office will fill in this part)

9923882.6

3. Full name, address and postcode of the or of each applicant (underline all surnames)

E. I. du Pont de Nemours & Company and Company
1007 Market Street
Wilmington
DE 19898
UNITED STATES OF AMERICA

(A/L dated)
1-11-99

460687001m²

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

U.S.A. / Delaware

4. Title of the invention

CHEMICAL COMPOSITION

5. Name of your agent (if you have one)

Carpmaels & Ransford

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

**43 Bloomsbury Square
London
WC1A 2RA**

Patents ADP number (if you know it)

83001

If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body

Yes

See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description	19
Claim(s)	2
Abstract	
Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents
(*please specify*)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

Carpmaels & Ransford
Carpmaels & Ransford

8th October 1999

12. Name and daytime telephone number of person to contact in the United Kingdom

Bruce R. Cockerton

0171 242 8692

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

CHEMICAL COMPOSITION

The present invention relates to conductor compositions and their use in the
5 manufacture of components, particularly heating elements, in microelectronic circuits. These compositions are of particular use in the manufacture of demisting elements in heated windows, for example in automotive backlights.

The use of thick-film conductors as components in hybrid microelectronic circuits
10 is well known in the electronics field. Compositions for the manufacture of such components usually take the form of a paste-like solid-liquid dispersion, where the solid phase comprises finely divided particles of a noble metal or a noble metal alloy or mixtures thereof and an inorganic binder. The liquid vehicle for the dispersion is typically an organic liquid medium. Additional materials may be added in small quantities (generally
15 less than about 3% by weight of the composition) to modify the properties of the composition and these include staining agents, rheology modifiers, adhesion enhancers and sintering modifiers.

The metals used in the preparation of thick-film conductor compositions are
20 typically selected from silver, gold, platinum and palladium. The metal can be used either in isolation or as a mixture which forms an alloy upon firing. Common metal mixtures include platinum/gold, palladium/silver, platinum/silver, platinum/palladium/gold and platinum/palladium/silver. The most common systems used in the manufacture of heating elements are silver and silver/palladium. The inorganic binder is typically a glass or glass-
25 forming material, such as a lead silicate, and functions as a binder both within the composition and between the composition and substrate onto which the composition is coated. Due to environmental considerations, the use of lead-containing binders is becoming less common and lead-free binders such as zinc or bismuth borosilicates are now often employed. The role of the organic medium is to disperse the particulate components
30 and to facilitate the transfer of the composition onto the substrate.

The consistency and rheology of the composition is adjusted to the particular method of application which may comprise screen printing, brushing, dipping, extrusion,

spraying and the like. Typically, screen printing is used to apply the composition. The pastes are usually applied to an inert substrate, such as an alumina, glass, ceramic, enamel or metal substrate, to form a patterned layer. The thick-film conductor layer is normally dried and then fired, usually at temperatures between about 600 and 900°C, to volatilise or
5 burn off the organic medium and sinter or melt the inorganic binder and the metal components.

It is, of course, necessary to connect the conductive pattern to the other components of the electronic circuit, such as the power source, resistor and capacitor networks,
10 resistors, trim potentiometers, chip resistors and chip carriers. This is generally achieved by using metal clips, typically comprising copper, which are soldered to the conductive layer, either directly onto the conductive pattern or onto a solderable composition which is overprinted onto the pattern (an "over-print"). An over-print is generally applied only in the region of the conductive pattern to which the metal clips are attached by solder, which
15 region is generally referred to as the "clip area". The ability to solder onto the electrically-conductive layer is an important parameter in the manufacture of heating elements since it removes the requirement for an over-print. However, the inorganic binder, which is important for binding the paste onto the substrate, can interfere with solder wetting and result in poor adhesion of the soldered metal clips to the conductive layer. The
20 requirements of high substrate adhesion and high solderability (or adhesion of the metal clips to the conductive pattern) are often difficult to meet simultaneously. US Patent No. 5,518,663 provides one solution to this problem by incorporating into the composition a crystalline material from the feldspar family.

25 An important application of patterned electrically-conductive layers is in the automobile industry, and particularly in the manufacture of windows which can be defrosted and/or demisted by an electrically-conductive grid permanently attached to the window and capable of producing heat when powered by a voltage source. In order for the window to defrost quickly, the circuit must be capable of supplying large amounts of
30 power from a low voltage power source, typically 12 volts. For such power sources the resistivity requirement of the conductive pattern is in the range of from about 2 to about 5 $\mu\Omega$ cm (5m Ω/\square at 10 μ m). This requirement is readily met by conductors containing

noble metals, particularly silver which is the most commonly-used material for this application.

In certain applications, a conductive layer having a higher resistivity is required. Furthermore, it is anticipated that the resistivity requirements of the conductive compositions used in window-heating elements in automobiles will shortly need to change since the automotive industry is expected to adopt the use of a 42 and 48 volt power supply in the near future. As a result, the window-heating elements will be required to exhibit higher values of resistivity, typically greater than about $10 \mu\Omega \text{ cm}$, preferably greater than about $12 \mu\Omega \text{ cm}$, and particularly in the range from about 20 to about $50 \mu\Omega \text{ cm}$.

A number of different materials may be added to adjust the specific resistivity of a conductive composition. For example, an increase in the content of precious metals such as platinum and palladium will increase the specific resistivity. Silver/palladium and silver/platinum compositions can achieve resistivity values from about $2 \mu\Omega \text{ cm}$ (that of a composition comprising only silver and binder) up to around $100 \mu\Omega \text{ cm}$ (for a 70:30 Pd:Ag blend). Such systems are, however, significantly more expensive and their use would be prohibitive in applications requiring coverage of a large surface area, such as the window-heating elements used in the automotive industry. In addition, an over-print of a composition containing a high amount of silver (and typically small amounts of filler) is generally required for certain metal blends, such as compositions containing high palladium levels, in order to achieve adequate solder adhesion. Conventional conductive compositions which typically operate at resistivity values of 2 to $5 \mu\Omega \text{ cm}$ and which are comprised predominantly of silver do not require an over-print since acceptable levels of solder adhesion can be achieved by adjusting the levels of inorganic binder.

Other, lower-cost approaches for achieving a high resistivity involve blending large amounts of filler into a silver-containing conductive composition to block the conductive path. Fillers are typically inorganic materials and those commonly used are glass (which may be the same or different as that used for the binder) and alumina (or other metal oxides). However, such approaches tend to result in a loss of solder acceptance and solder adhesion. For example, adequate solder adhesion can be maintained only up to a level of about 10% alumina by weight of the composition but this level is generally too low for an

appreciable rise in resistivity. For glass-type fillers, loss of solder adhesion occurs at even lower levels and, again, this level is too low for an appreciable rise in resistivity. In addition, this problem can not normally be ameliorated by the use of silver over-prints owing to glass migration between the layers during firing, specifically from the conductive
5 coating into the over-print.

A further requirement of the conductor compositions is that they must be chemically durable and resilient to exposure to varying environmental conditions such as temperature, humidity, acid and salt. Compositions comprising large amounts of glass
10 filler, particularly lead-free glass filler, are often relatively unstable to such factors.

An additional consideration is that it is desirable for the resistance of the coating composition to be substantially independent of the temperature of firing used in the manufacture of the patterned conductive layer. In particular, the behaviour of the
15 composition under sintering and melting should remain substantially constant between the temperatures of about 620 and 680°C. Nevertheless, a change in resistance of up to about 10% between these two temperatures, which corresponds to the behaviour of a pure silver composition, is generally tolerated. The use of large amounts of filler to significantly increase resistivity results in compositions which do not generally satisfy this requirement.

20 A further additional consideration is that it is desirable for the relationship between the resistivity and the amount of resistivity modifier added to the composition to be relatively predictable and/or substantially linear within the target range of desired resistivities. The resistivity of compositions comprising large amounts of filler generally
25 increases in an almost linear manner until a critical concentration is reached. At this critical concentration, the resistivity may rise very rapidly, often by an order of magnitude, when the level of resistivity modifier is increased by only a fraction of a weight percent. As a result, it is difficult to target specific values of resistivity for such compositions.

30 It is an object of this invention to provide higher-resistivity electrically-conductive compositions which do not suffer from the afore-mentioned disadvantages. In particular, it is an object of this invention to provide an economical electrically-conductive coating

composition having increased resistivity while at the same time exhibiting good solderability.

Accordingly, the present invention provides a composition comprising finely
5 divided particles of (a) an electrically-conductive material; (b) one or more inorganic binders; and (c) tin, wherein components (a), (b) and (c) are dispersed in an organic medium.

The compositions of the present invention are suitable for use as paste
10 compositions for forming thick-film conductive patterns on a substrate, for instance, by the process of screen-printing. The compositions of the present invention are of particular use in the manufacture of windows which can be defrosted and/or demisted by an electrically-conductive grid attached to the window, particularly for use in the automotive industry.

15 As used herein, the term "finely divided" is intended to mean that the particles are sufficiently fine to pass through a 400-mesh screen (US standard sieve scale). It is preferred that substantially all of the particles are in the size range of 0.01 to 20 μ m. Preferably, the largest dimension of substantially all particles is no more than about 10 μ m and desirably no more than about 5 μ m.

20

Preferably, the components are present in amounts such that the total amount of components (a), (b) and (c) is about 50 to about 95% by weight of the composition, with the organic medium being present in amounts of about 5 to about 50% by weight of the composition. In a preferred embodiment, the total amount of components (a), (b) and (c) is
25 in the range from about 60 to about 90 %, preferably from about 70 to about 85% by weight of the composition.

Compounds (a), (b) and (c) generally comprise substantially all of the solid phase material used to prepare the compositions of the invention. Preferably component (a) is
30 present in amounts of from about 30 to about 99.4%, preferably from about 50 to about 98%, and more preferably from about 60 to about 90%, by weight of the total solids present in the composition. Preferably component (b) is present in amounts of from about 0.5 to about 40%, preferably from about 2 to about 20% and more preferably from about 5

to about 15%, by weight of the total solids present in the composition. Preferably component (c) is present in amounts of about 0.1 to about 30%, preferably from about 2 to about 20%, and more preferably from about 4 to about 16% by weight of the total solids present in the composition.

5

The electrically-conductive particles of component (a) can be in any form suitable for the production of the compositions of the present invention. For example, electrically-conductive metallic particles may be in the form of either metal powders or metal flakes or blends thereof. In a preferred embodiment of the invention, the metallic particles are a
10 blend of powder and flake. The particle size of the metal powder or flake is not by itself narrowly critical in terms of technical effectiveness. However, particle size does affect the sintering characteristics of the metal in that large particles sinter at a lower rate than small particles. Blends of powders and/or flakes of differing size can be used to tailor the sintering characteristics of the conductor formulation during firing, as is well-known in the
15 art. The metal particles should, however, be of a size that is appropriate to the method of application thereof, which is usually screen printing. The metal particles should therefore generally be no larger than about 20 μ m in size and preferably less than about 10 μ m. The minimum particle size is normally about 0.1 μ m.

20 The preferred metal for the electrically-conductive component (a) of the conductor composition of the present invention is silver. Silver particles larger than about 1.0 μ m impart greater colouring to the composition. It is preferred that the compositions of the invention contain at least 50% weight silver particles larger than 1.0 μ m. The silver will ordinarily be of high purity, typically greater than 99% pure. However, less pure materials
25 can be used depending on the electrical requirements of the conductive layer or pattern. In an embodiment of the invention, component (a) comprises a mixture of silver and nickel and/or suitable derivatives. A preferred nickel derivative suitable for use in this embodiment of the invention is nickel boride (Ni₃B). Typically, the Ag:Ni ratio will be about 1:1 to about 25:1, preferably at least about 1.5:1 and more preferably about 1.5:1 to
30 about 3:1.

Component (c) in the compositions of the present invention comprises metallic tin particles. In one embodiment of the invention, component (c) may comprise a derivative

of tin which is substantially converted to the metal under the action of heat. Metallic tin particles are preferred. The size of the tin particles should generally be no larger than about $20\mu\text{m}$ and preferably less than $10\mu\text{m}$. The minimum particle size is normally about $0.1\mu\text{m}$.

5

The use of tin particles as an additive according to the present invention provides compositions which exhibit (i) high resistivity; (ii) high solder adhesion; (iii) a more uniform rise in resistivity with increasing concentration of the additive in relation to compositions in which large amounts of filler are used to increase resistivity; and (iv) low variation of resistance with firing temperature. In addition, tin is a relatively inexpensive material and is an economical method of increasing resistivity.

Suitable inorganic binders for use in the present invention are those materials which upon sintering serve to bind the metal to a substrate such as glass or ceramic or alumina substrates. The inorganic binder, also known as a frit, comprises finely-divided particles and is a key component in the compositions of the present invention. The softening point and viscosity of the frit during firing, as well as its wetting characteristics for the metal powder/flake and the substrate, are very important factors. The particle size of the frit is not narrowly critical and frits useful in the present invention will typically have an average particle size from about 0.5 to about $4.5\mu\text{m}$, preferably from about 1 to about $3\mu\text{m}$.

It is preferred that the inorganic binder is a frit having a softening point of between about 350 and 620°C in order that the compositions can be fired at the desired temperatures to effect proper sintering, wetting and adhesion to the substrate. It is known that mixtures of high and low melting frits can be used to control the sintering characteristics of the conductive particles. In particular, it is believed that the high temperature frit dissolves in the lower melting frit and together they slow the sintering rate of the conductive particles as compared to pastes containing only low melting frit. This control of the sintering characteristics is especially advantageous when the composition is printed and fired over decorative enamels. (Decorative enamels are normally pastes comprised of one or more pigment oxides and opacifiers and glass frit dispersed in an organic medium.) A high melting frit is considered to be one having a softening point above 500°C and a low melting frit is considered to be one having a softening point below

500°C. The difference in the melting temperatures of the high and low melting frits should be at least 100°C and preferably at least 150°C. Mixtures of three or more frits having different melting temperatures can also be used. When mixtures of high and low melting frits are used in the invention, they are normally used in ratios by weight from 4:1 to 1:4.

5

As used herein, the term "softening point" refers to softening temperatures obtained by the fibre elongation method of ASTM C338-57.

Suitable binders include lead borates, lead silicates, lead borosilicates, cadmium
10 borate, lead cadmium borosilicates, zinc borosilicates, sodium cadmium borosilicates, bismuth silicates, bismuth borosilicates, bismuth lead silicates and bismuth lead borosilicates. Typically, any glass having a high content of bismuth oxide, preferably at least 50 % and more preferably at least 70 % by weight bismuth oxide, is preferred. Lead oxide as a separate phase may also be added, if necessary. However, due to environmental
15 considerations, lead-free binders are preferred. Examples of glass compositions (compositions A to I) are given in Table 1 below; the oxide components are given in weight percent.

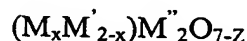
Table 1 – Glass Compositions

	A	B	C	D	E	F	G	H	I
Bi ₂ O ₃	75.1	82.7			78.1	94.8	73.3	73.7	69.82
PbO	10.9	1.83	43.6	0.7					
B ₂ O ₃	1.2	1.34	4.8	26.7					8.38
SiO ₂	9.3	10.3	37.5	21.7	8.6	5.2	4.7	4.8	7.11
CaO	2.4	2.68	9.7	4.0					0.53
BaO				0.9					
ZnO				27.6	3.9			5.0	12.03
CuO					7.6		5.5		
CoO					1.8				
Al ₂ O ₃	1.1	1.22	4.3	5.7					2.13
Na ₂ O				8.7					
ZrO ₂				4.0					
GeO ₂							16.5	16.6	

The glass binders are prepared by conventional glass-making techniques, by mixing the desired components (or precursors thereof, e.g., H₃BO₃ for B₂O₃) in the desired proportions and heating the mixture to form a melt. As is well known in the art, heating is conducted to a peak temperature and for a time such that the melt becomes entirely liquid, yet gaseous evolution has ceased. The peak temperature is generally in the range 1100°C-1500°C, usually 1200°C-1400°C. The melt is then quenched by cooling the melt, typically by pouring onto a cold belt or into cold running water. Particle size reduction can then be accomplished by milling as desired.

Other transition metal oxides may also be employed as part of the inorganic binder, as is well known to those skilled in the art. Oxides or oxide precursors of zinc, cobalt, copper, nickel, manganese and iron are commonly used, particularly with substrates other than glass substrates, such as alumina substrates. These additives are known to improve soldered adhesion.

The inorganic binder can also contain up to approximately 4 parts by weight basis paste of a pyrochlore-related oxide having the general formula:



5 wherein

M is selected from at least one of Pb, Bi, Cd, Cu, Ir, Ag, Y and rare earth metals having atomic numbers of 57-71 and mixtures thereof,

M' is selected from Pb, Bi and mixtures thereof,

M'' is selected from Ru, Ir, Rh and mixtures thereof,

10 X=0-0.5, and

Z=0-1.

Pyrochlore materials have been described in detail in US Patent No. 3,583,931, the disclosure of which is incorporated herein by reference. The pyrochlore materials act as adhesion promoters for the compositions of this invention. Copper bismuth ruthenate
15 $(Cu_{0.5}Bi_{1.5}Ru_2O_{6.75})$ is preferred.

Traditionally, conductive compositions have been based on lead frits. The elimination of lead from glass compositions to meet current toxicity and environmental regulations may limit the types of binder that can be used to achieve the desired softening
20 and flow characteristics, while simultaneously meeting wettability, thermal expansion, cosmetic and performance requirements. US Patent No. 5,378,406, the disclosure of which is incorporated herein by reference, describes a series of low-toxicity lead-free glasses based upon the constituents Bi_2O_3 , Al_2O_3 , SiO_2 , CaO , ZnO and B_2O_3 , all of which may be used in the compositions of the present invention.

25

In a preferred embodiment of the invention, the frit is composition I in Table 1 herein.

The components (a) to (c) of the composition hereinbefore described will ordinarily
30 be dispersed into an organic medium to form a semi-fluid paste which is capable of being printed in a desired circuit pattern. Any suitably inert liquid can be used as organic medium (vehicle for the production of this paste), non-aqueous inert liquids being preferred. The organic medium should provide acceptable wettability of the solids and the

substrate, a relatively stable dispersion of particles in the paste, good printing performance, dried film strength sufficient to withstand rough handling, and good firing properties. Various organic liquids with or without thickening agents, stabilising agents and/or other common additives are suitable for use in the preparation of the compositions of the present invention. Exemplary of the organic liquids which can be used are alcohols; esters of such alcohols such as the acetates and propionates; terpenes such as pine oil, terpineol and the like; solutions of resins such as polymethacrylates of lower alcohols; or solutions of ethyl cellulose in solvents such as pine oil and monobutyl ether of ethylene glycol monoacetate. The medium can also contain volatile liquids to promote fast setting after application to the substrate.

A preferred organic medium is based on a combination of a thickener consisting of ethyl cellulose in terpineol (ratio 1 to 9), combined with the monobutyl ether of ethylene glycol monoacetate sold under the trade name butyl Carbitol acetate. A further preferred organic medium is based on ethyl cellulose resin and a solvent mixture of alpha-, beta- and gamma-terpineols (typically 85-92% alpha-terpineol containing 8-15% beta and gamma-terpineol).

The ratio of organic medium to solids in the dispersion can vary considerably and is determined by the final desired formulation viscosity which, in turn, is determined by the printing requirements of the system. Normally, in order to achieve good coverage, the dispersions will contain about 50 to about 95%, preferably about 60 to about 90%, by weight solids, and about 5 to about 50%, preferably about 10 to about 40%, by weight organic medium, as noted above.

The compositions of the present invention may additionally comprise further additives known in the art, such as colorants and staining agents, rheology modifiers, adhesion enhancers, sintering inhibitors, green-state modifiers, surfactants and the like.

In the preparation of the compositions of the present invention, the particulate inorganic solids are mixed with the organic medium and dispersed with suitable equipment, such as a three-roll mill or a power-mixer, according to conventional techniques well-known in the art, to form a suspension. The resulting composition has a

viscosity preferably in the range of about 10-200, preferably in the range of about 15-100 Pa.s at a shear rate of 4 sec^{-1} , for instance, as measured on a Brookfield HBT viscometer using #5 spindle at 10 rpm and 25°C . The general procedure for preparing the composition of the invention is set out below.

5

The ingredients of the paste are weighed together in a container. The components are then vigorously mixed by a mechanical mixer to form a uniform blend; then the blend is passed through dispersing equipment, such as a three-roll mill, to achieve a good dispersion of particles to produce a paste-like composition having a suitable consistency and rheology for application onto a substrate, for instance by screen-printing. A Hegman
10 gauge is used to determine the state of dispersion of the particles in the paste. This instrument consists of a channel in a block of steel that is $25 \mu\text{m}$ deep (1 mil) on one end and ramps up to zero depth at the other end. A blade is used to draw down paste along the length of the channel. Scratches appear in the channel where the agglomerates' diameter is
15 greater than the channel depth. A satisfactory dispersion will give a fourth scratch point of typically $10\text{-}18 \mu\text{m}$. The point at which half of the channel is uncovered with a well-dispersed paste is between $3 \text{ and } 8 \mu\text{m}$ typically. Fourth scratch measurements of $>20 \mu\text{m}$ and "half-channel" measurements of $>10 \mu\text{m}$ indicate a poorly dispersed suspension.

20 The compositions are then applied to a substrate, such as glass or alumina ceramic, using conventional techniques known in the art, typically by the process of screen printing, to a wet thickness of about $20\text{-}60 \mu\text{m}$, preferably about $35\text{-}50 \mu\text{m}$. The compositions of this invention can be printed onto the substrates either by using an automatic printer or a hand printer in the conventional manner. Preferably, automatic screen printing techniques
25 are employed using a 200- to 325-mesh screen. The printed pattern is then dried at below 200°C , preferably at about 150°C , for about 5-15 minutes before firing. Firing to effect sintering of both the inorganic binder and the finely divided particles of metal is preferably done in a well-ventilated belt conveyor furnace with a temperature profile that will allow burn-off of the organic matter at about $200^{\circ}\text{-}500^{\circ}\text{C}$, followed by a period of maximum
30 temperature of about $500\text{-}1000^{\circ}\text{C}$, preferably about $600\text{-}850^{\circ}\text{C}$, lasting about 5-15 minutes followed by a cooldown cycle, optionally a controlled cooldown cycle, to prevent over-sintering, unwanted chemical reactions at intermediate temperatures or substrate fracture which can occur from too rapid cooldown. The overall firing procedure will preferably

extend over a period of about 30-60 minutes, with 10-25 minutes to reach the firing temperature, about 10 minutes at the firing temperature and about 10-25 minutes in cooldown. In some instances, total cycle times can be used as short as 20-30 minutes by conventional firing and 1-14 minutes using infrared firing.

5

Typical thicknesses of the thick-films after firing are from about 3 μm to about 40 μm , preferably from about 8 μm to about 20 μm

The compositions of the invention are primarily intended for use in the manufacture
10 of heating elements in windows such as defogging or defrosting elements in automotive
backlights. However, the coating compositions can be employed in various other
applications, including printed circuits and heating elements generally. For instance, the
compositions of the present invention may be used as base plates in hot water heating
appliances. There is a general need within the electronics and electrical industry for lower-
15 cost heating elements, particularly screen-printable heating elements.

According to a further aspect of the invention, there is provided a composition
comprising finely divided particles of (a) an electrically-conductive material; (b) one or
more inorganic binders; and (c) tin, wherein components (a), (b) and (c) are dispersed in an
20 organic medium, for use in the manufacture of an electrically-conductive pattern on a
substrate.

According to a further aspect of the invention, there is provided a process for the
preparation of a composition comprising finely divided particles of (a) an electrically-
25 conductive material; (b) one or more inorganic binders; and (c) tin, said process
comprising the step of dispersing components (a), (b) and (c) in an organic medium.

According to a further aspect of the invention there is provided a process for the
manufacture of an electrically-conductive pattern, said process comprising applying to a
30 substrate a composition comprising finely divided particles of (a) an electrically-
conductive particles; (b) one or more inorganic binders; and (c) tin, said components (a),
(b) and (c) being dispersed in an organic medium, and firing the coated substrate to effect

sintering of the finely-divided particles to the substrate. Preferably the process is a screen printing process.

According to a further aspect of the present invention there is provided a substrate,
5 typically a rigid substrate such as a glass, ceramic, alumina or metal substrate, having on one or more surfaces thereof an electrically-conductive pattern, said conductive pattern comprising (a) an electrically-conductive material; (b) one or more inorganic binders; and (c) tin.

10 The following test procedures were used to evaluate the compositions of the present invention.

Adhesion

Copper clips (obtained from Quality Product Gen. Eng. (Wickwar), UK) are
15 soldered to the fired conductive pattern on a glass substrate (dimensions 4"x 2"x 3mm) using a 70/27/3 Pb/Sn/Ag solder alloy at a soldering iron temperature of 350 to 380°C. A small quantity of a mildly active rosin flux, such as ALPHA 615-25® (Alpha Metals Limited, Croydon, U.K.) may be used to enhance solder wetting and to keep the solder and clip in place during assembly of parts, in which case the flux is applied to the solder using
20 a shallow tray containing a thin film of fresh flux. Adhesion was measured on a Chattillon® pull tester Model USTM at a pull speed of 0.75 ± 0.1 inches per minute and the pull strength recorded at adhesion failure. The average value of adhesion failure over 8 samples was determined. Adhesion values of greater than 20 Kg are preferred. The principal failure modes of adhesion are as follows:

- 25 (a) clip separates from the conductive pattern (i.e. poor solder adhesion).
- (b) the conductive pattern separates from the substrate (i.e. poor substrate adhesion).
- (c) glass pullout/fracture (i.e. the bonding strengths between the clip and the conductive layer and between the conductive layer and the substrate is greater than the strength of the substrate).
- 30 (d) failure within the solder.

Resistance and Resistivity

The resistance of the fired conductive pattern on a glass substrate (dimensions 4"x2"x3mm) is measured using a GenRad Model 1657 RLC bridge calibrated for use between 1 and 10 Ω or equivalent. The thickness of the conductive layer is measured using a thickness measuring device such as a surf-analyser (e.g. TALYSURF, which is a contact measuring device which analyses the surface of the substrate in 2 dimensions using a spring loaded stylus; any change in height will deflect the stylus and this change will then be registered on a recorder, such as a chart recorder; the difference between the base line and average height gives the print thickness). Resistance of the pattern is determined by placing the probe tips at the point where the conductive track meets the solder pads. The bulk resistivity (thickness-normalised) of the layer is determined by dividing the measured resistance for the pattern by the number of squares therein where the number of squares is the length of the conductive track divided by the width of the track. The resistivity value is obtained as $m\Omega/\square$ at any normalised thickness, typically 10 μ m.

Particle Size

Particle size in the composition is measured according to ASTM D1210-79 using a large Hegman type fineness of grind gauge.

Chemical Durability

A solution of 1% glacial acetic acid in deionised water is used in this test. The glass substrate (50 x 100mm) having thereon a fired conductive pattern was inserted into a plastic container half-filled with the test solution. The container is then sealed and left to stand at ambient temperature. The test substrates are removed after 96, 168 and 336 hours, dried and then analysed by a lift test. The lift test comprises application of a 15mm wide masking tape onto the substrate and then removing sharply in approximately 1/2 second. The results of the lift test are given as the approximate percentage of film area removed by the tape.

The invention will now be described with reference to the following examples. It will be appreciated that the examples are not intended to be limiting and modification of detail can be made without departing from the scope of the invention.

EXAMPLES

A series of conductive patterns were prepared using the method hereinbefore described. The tin particles used were -325 mesh tin particles. The substrate was a float glass (non-tempered) substrate. The fired film thickness was from 8 to 20 μ m. All parts
5 were fired through a belt furnace with a peak firing temperature of 660°C, unless otherwise specified, with the samples spending approximately 72 s at peak temperature. The total door-to door transit time in the furnace was approximately 21 minutes.

The resistivity, solder adhesion, chemical durability and resistance/firing
10 temperature relationship of the patterns were measured as a function of composition in accordance with the procedures described above and the results are shown in Tables 2, 3 and 4 below.

Table 2 – Adhesion Strength (W) and resistivity (ρ) as a function of composition

Example	Silver (% w/w)	Glass (% w/w)	Tin (% w/w)	ρ ($\mu\Omega$ cm)	W (Kg)
A	80	4	0.00	3.68	26
B	69.83	13.66	0.00	4.27	3
C	62.73	20.97	0.00	5.66	1
D	55.04	28.88	0.00	6.93	0
E	47.57	36.57	0.00	9.49	0
F	39.22	45.17	0.00	15.54	0
G	30.66	53.98	0.00	28.42	0
1	79.15	4.00	0.80	5.49	31
2	77.46	4.00	2.40	6.84	26
3	75.76	4.00	4.00	10.29	23
4	73.22	4.00	6.40	16.20	20
5	71.51	4.00	8.00	23.46	17
6	67.26	4.00	12.00	75.28	11
7	63.03	4.00	16.00	314.22	10
8	72.00	3.60	8.00	13.11	18
9	70.30	5.00	8.00	13.78	18
10	69.08	6.00	8.00	14.02	19
11	67.86	7.00	8.00	15.48	18
12	66.65	8.00	8.00	16.30	22
13	65.42	9.00	8.00	16.32	20
14	64.21	10.00	8.00	17.68	20
15	58.13	15.00	8.00	26.29	19

Table 3 – Stability of resistance to variation of firing temperature as a function of composition

Example	Silver (% w/w)	Glass (% w/w)	Tin (% w/w)	R (Ω)				$\Delta R/R_{620}$ (%)
				620°C	640°C	660°C	680°C	
A	80	4	0	3.47	3.27	3.13	3.15	9.3
H	53	25	0	10.03	9.32	9.10	8.91	11.2
I	40	37	0	16.80	17.28	18.29	10.30	38.7
2	77.46	4.00	2.40	3.76	3.74	3.66	3.44	9.0
4	73.22	4.00	6.40	9.71	9.97	10.07	9.85	1.4
8	72.00	3.60	8.00	9.18	8.62	8.74	8.47	7.7
9	70.30	5.00	8.00	10.96	10.54	10.42	10.25	6.5
10	69.08	6.00	8.00	11.56	11.07	10.66	10.61	8.2
12	66.65	8.00	8.00	13.26	12.57	12.19	12.01	9.4
13	65.42	9.00	8.00	14.30	13.49	12.92	12.76	10.8
14	64.21	10.00	8.00	16.32	15.40	14.19	14.44	11.5
15	58.13	15.00	8.00	25.13	23.52	21.90	21.73	13.5

5 Table 4 – Chemical Durability as a function of composition

Example	Silver (% w/w)	Glass (% w/w)	Tin (% w/w)	Acid durability (@ 96 hrs)	Acid durability (@ 168 hrs)	Acid durability (@ 336 hrs)
A	80.00	4.00	0.00	pass	fail	fail
1	79.15	4.00	0.80	pass	70%	<95%
2	77.46	4.00	2.40	pass	60%	<70%
3	75.76	4.00	4.00	pass	40%	<50%
4	73.22	4.00	6.40	pass	10%	<10%
5	71.51	4.00	8.00	pass	5%	<10%
6	67.26	4.00	12.00	pass	pass	pass
7	63.03	4.00	16.00	pass	pass	pass

The data demonstrate that the tin-containing compositions of the present invention
 10 have the following advantages in the preparation of conductive patterns:

- (i) They allow the preparation of conductive patterns which exhibit increased resistivity while maintaining solder adhesion.
- (ii) They allow the preparation of conductive patterns which, for a given increase in resistivity, exhibit a smaller variation of resistance with variation of firing temperature.
- (iii) They allow the preparation of conductive patterns having a greater degree of chemical durability.
- (iv) They allow the preparation of conductive compositions in which the resistivity versus the amount of resistivity modifier is more predictable and/or linear within the target range of desired resistivities.

CLAIMS

1. A composition comprising finely divided particles of (a) an electrically-conductive material; (b) one or more inorganic binders; and (c) tin, wherein components (a),
5 (b) and (c) are dispersed in an organic medium.
2. A composition according to claim 1 wherein said electrically-conductive particles are silver particles.
- 10 3. A composition according to claim 1 or 2 wherein said electrically-conductive particles are a blend of flake and powder.
4. A composition according to claim 1, 2 or 3 wherein substantially all particles are in the range of 0.01 to 20 μm .
- 15 5. A composition according to any preceding claim wherein the total amount of components (a), (b) and (c) is about 50 to about 95 % by weight of the composition.
6. A composition according to any preceding claim wherein component (a) is present
20 in amounts of about 60 to about 99 % by weight of the total solids present in the composition.
7. A composition according to any preceding claim wherein component (b) is present in amounts of about 0.5 to about 30 % by weight of the total solids present in the
25 composition.
8. A composition according to any preceding claim wherein component (c) is present in amounts of about 0.5 to about 25 % by weight of the total solids present in the
30 composition.
9. A composition according to any preceding claim wherein the inorganic binder is lead-free.

10. A composition according to any preceding claim which is screen-printable.
11. A composition according to any preceding claim for use in the manufacture of an
5 electrically-conductive pattern on a substrate.
12. A process for the manufacture of an electrically-conductive pattern, said process
comprising applying to a substrate a composition comprising finely divided
particles of (a) an electrically-conductive material; (b) one or more inorganic
10 binders; and (c) tin, said components (a), (b) and (c) being dispersed in an organic
medium, and firing the coated substrate to effect sintering of the finely-divided
particles to the substrate.
13. A process according to claim 12 which is a screen-printing process.
15
14. An article comprising a substrate having on one or more surfaces thereof an
electrically-conductive pattern, said conductive pattern comprising (a) an
electrically-conductive material; (b) one or more inorganic binders; and (c) tin.

